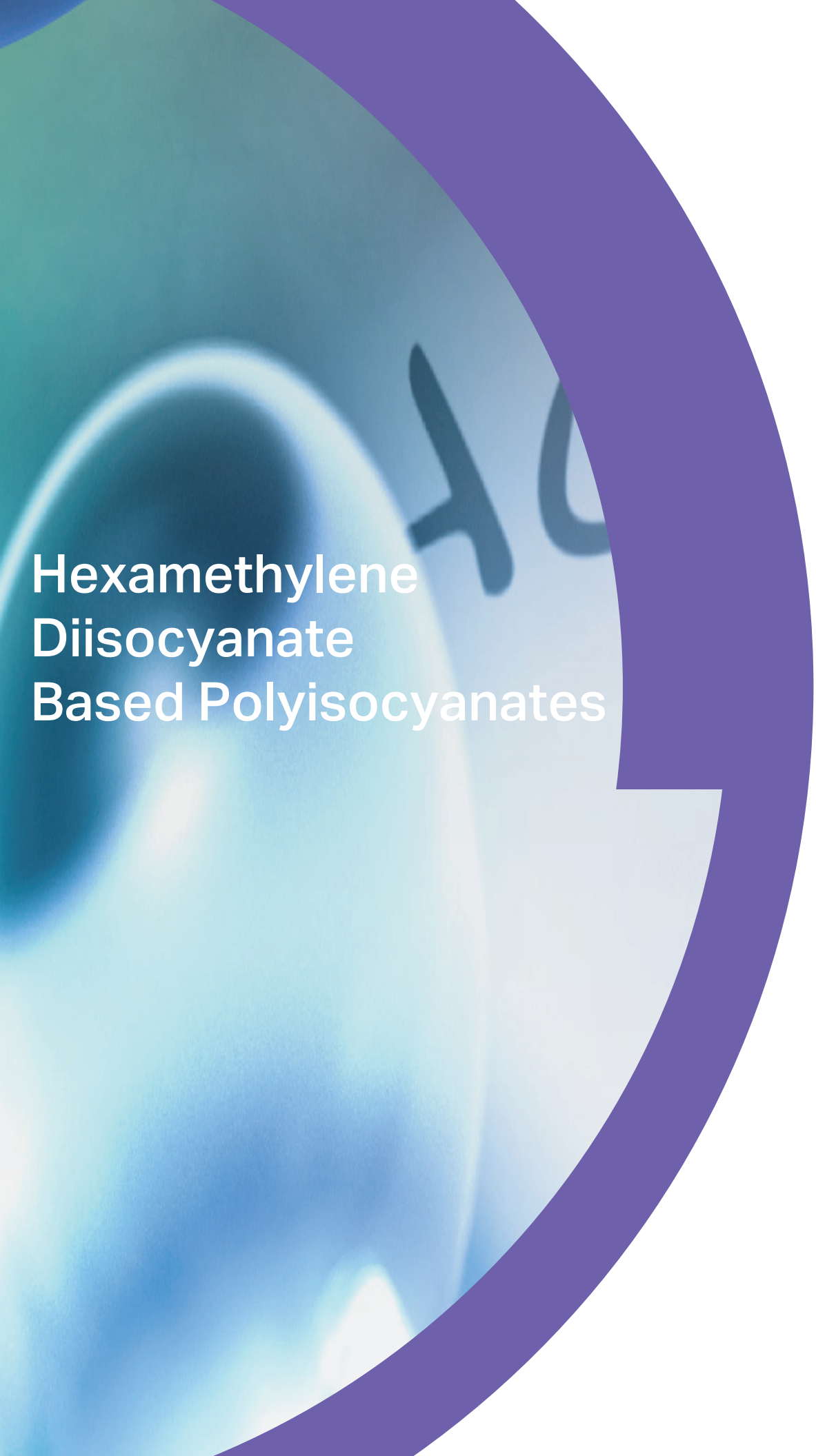

covestro

Hexamethylene Diisocyanate Based Polyisocyanates

Desmodur® N

Introduction

Polyisocyanates based on HDI (hexamethylene diisocyanate) represent a very important class of polyisocyanates used in formulating polyurethane coatings. This is a group of clear, slightly yellow, liquid aliphatic polyisocyanate resins that are sold as 100% solids resins or dissolved in various solvents. The viscosities of the resins vary depending on the product.

These Covestro products, used as raw materials for polyurethane coatings, are polyisocyanates produced from HDI (See Figure 1). From this product group, most important are the biuret types -- Desmodur® N 75A BA/X, Desmodur N 100A and Desmodur N 3200A (See Figure 2), the isocyanurate types -- Desmodur N 3390A BA/SN and Desmodur N 3300A (See Figure 3), and the water dispersible types -- Bayhydur 302 and Bayhydur 303. At the time of manufacture, all products contain a small amount of HDI monomer. The isocyanurate types and the water dispersible types, with a content of residual monomeric diisocyanate below 0.3 weight percent (calculated on polyisocyanate), remain stable during storage. The monomer content of the biuret types, which is below 0.7 weight percent (calculated on polyisocyanate) at time of manufacture, may raise to 1.6 weight percent (calculated on polyisocyanate) during storage, with the degree of increase being highest at elevated temperatures.

Both the polyisocyanate and the monomer have toxicological importance. In addition, solvents are contained in some of the products and contribute to the overall toxicity of the product.

Persons who handle or work with HDI based polyisocyanates must be familiar with the potential risks involved and must be trained in the safe use and handling of these materials. Covestro's Product Safety Regulatory Affairs (PSRA) Department can provide assistance in understanding the hazards and in developing proper handling procedures. This brochure provides information on the human health effects and toxicity of these products, recommendations for medical procedures, safe handling practices, industrial hygiene monitoring and analysis techniques, and proper storage and disposal methods. Further details may be found in the Safety Data Sheet (SDS) specific to each HDI based polyisocyanate.

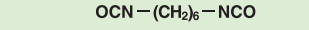

Figure 1: Hexamethylene Diisocyanate (HDI)

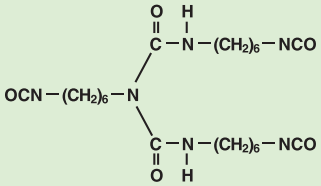

Figure 2: The biuret of HDI

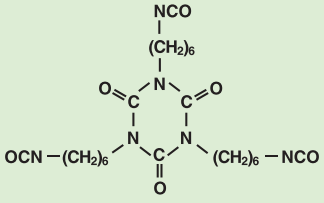

Figure 3: The isocyanurate ring of HDI

Health Effects

Diisocyanates/Polyisocyanates

Major effects of overexposure to HDI based polyisocyanates include:

- Irritation of the lungs, skin and eyes
- Sensitization (skin and lungs)

In addition, chronic overexposure to isocyanates has been reported to cause lung damage, including a decrease in lung function. Lung damage and sensitization may be permanent.

To protect the worker against airborne exposures to chemicals, the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) have established, respectively, Permissible Exposure Limits (PELs) or Threshold Limit Values (TLVs) for a number of chemicals. According to ACGIH: TLVs "...refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse health effects."

The ACGIH has established a Threshold Limit Value (TLV) for hexamethylene diisocyanate (HDI) monomer of 0.005 ppm as an eight hour time weighted average (TWA). Although PELs have been established for several of the diisocyanates, federal OSHA has not established one for HDI. Covestro endorses the ACGIH TLV-TWA, and, in addition, recommends a Ceiling level (C) for HDI of 0.02 ppm (Manufacturer's Guideline Level, MGL). This concentration should not be exceeded even for brief periods.

ACGIH and federal OSHA have not established a TLV or PEL for the HDI polyisocyanates. However, the recommended Manufacturer's Guideline Level (MGL) for the HDI based polyisocyanates is 0.5 mg/m^3 as an eight hour time weighted average (TWA) and a 1.0 mg/m^3 short term exposure limit (STEL - averaged over 15 minutes).

Irritation

Toxicological research as well as practical experience have shown that diisocyanates can cause irritation of the skin, respiratory tract (nose, throat, lungs) and eyes. Irritation is an acute response which results from direct contact with isocyanates, i.e., skin protein and moisture, mucous membranes of the nasal passages, throat and respiratory tract, eyes, etc. Skin symptoms include reddening, swelling, rash, scaling or blistering. Blisters may appear as a result of prolonged contact. Symptoms of eye irritation include pain, reddening, tearing, and swelling accompanied by a stinging sensation and/or feeling of fine dust in the eyes. Chronic eye overexposure may result in corneal opacity (clouding of the eye surface).

Irritation caused by HDI has been observed by some individuals at airborne levels of about 50 to 100 parts per billion (ppb). Extensive overexposure to high concentrations of HDI monomer or polyisocyanate (whether in the form of vapor or aerosol) well above the guidelines (such as can occur during improper spraying in an unventilated or confined space without proper respiratory protection) may lead to bronchitis, bronchial spasm, and pulmonary edema (fluid in the lungs). The amount of irritation is dependent upon the concentration, the tissue exposed, and individual susceptibility, but it generally is independent of the individual's

exposure history. Chemical or hypersensitivity pneumonitis, with flu-like symptoms (i.e., fever, chills) have also been reported. These acute symptoms are generally reversible soon after removal of the person from the contaminated environment or, in case of skin contact, removal of the isocyanate from the skin. Persons with a pre-existing, non-specific bronchial hyper-reactivity can respond with asthmatic symptoms at concentrations below the recommended limits. Although animal studies demonstrate that HDI products have low oral toxicity, ingestion (swallowing) can cause irritation to the mouth, stomach and digestive tract. However, ingestion is not considered a common route of exposure in an industrial setting.

Sensitization

Sensitization, resulting in allergic dermatitis or asthmatic symptoms, can occur following overexposure to isocyanates. Experience has shown that polyisocyanates may have a reduced potential to cause irritation and sensitization relative to their monomeric precursors.

Sensitization is a systemic response and is not limited to the area of contact. Sensitization usually does not occur on initial exposure but can develop within the first few months of employment in an isocyanate containing environment. Sensitization may develop as a result of repeated overexposure or a single large dosage, e.g., from a spill or other accident. The onset of respiratory and dermal sensitization depends upon the applied concentration, properties of the isocyanate, route of exposures and the individual's susceptibility. Exposures subsequent to the exposure(s) which actually resulted in sensitization can cause a very strong allergic reaction. A sensitized individual may react to extremely low airborne levels, well below the TLV, PEL or MGL. Once a person is sensitized and is again exposed, the symptoms of respiratory sensitization may develop immediately or after a delay of serveral hours, or both.

In the case of respiratory sensitization, the response is similar to asthma, i.e., coughing, wheezing, tightness in the chest and shortness of breath. Respiratory sensitization may be either temporary or permanent. Similar to many non-specific asthmatic responses, there are reports that once sensitized, an individual can react to dust, cold air or other irritants. This increased lung sensitivity can persist for weeks and in severe cases for several years.

Inhalation Sensitization

- React to Low Levels
- Asthma-like Symptoms
- Immediate or Delayed
- Other Sensitivities May Develop
- May be Long Lasting
- Temporary or Permanent

Chronic overexposure to monomeric diisocyanate (e.g., toluene diisocyanate, TDI) also have been reported to cause lung damage, including decrease in lung function, which may be permanent.

The skin sensitization reaction is allergic dermatitis which may include symptoms such as rash, itching, hives, and swelling of the arms and legs. A person with dermal sensitization may experience a skin reaction even if he is being exposed to airborne (vapor) isocyanate.

There is some evidence for cross-sensitization among isocyanates. This means that an individual could develop sensitivity to, for example, toluene diisocyanate (TDI) and then react upon exposure to a different diisocyanate (e.g., HDI).

Solvents

Some HDI based products manufactured by Covestro contain solvents. In some cases, solvents may be added by the user to change the viscosity. Prolonged or repeated overexposure to these solvents, either by inhalation or direct skin contact, may also cause adverse health effects. The effects are dependent upon the solvent, the extent of exposure and the route of exposure. Hence, it is important to refer to the Safety Data Sheet for the health hazards relating to the specific solvent or solvents that are to be used.

In general, solvent vapors may be irritating to the skin, eyes, nose, throat and lungs. Symptoms of irritation may include: redness, burning and itching of the eyes, dryness of the throat and tightness of the chest. Other possible symptoms of overexposure include: headache, nausea, narcosis, fatigue, loss of appetite and other gastrointestinal disturbance.

Chronic overexposure to organic solvents has been associated with various neurotoxic effects, including permanent brain and nervous system damage. Symptoms include: loss of memory, loss of intellectual ability or loss of coordination. In addition, reports have associated repeated and prolonged occupational overexposure to solvents with permanent brain and nervous system damage. Intentional misuse by deliberately concentrating and inhaling solvents may be harmful or even fatal.

Repeated or prolonged skin contact with solvents can result in dry, defatted and cracked skin, compromising its protective mechanism and thus causing increased susceptibility to infection and to solvent penetration. In addition, skin irritation (i.e., redness, swelling) which can develop into dermatitis, may occur from skin contact. Solvents can penetrate the skin and may cause systemic effects such as liver, kidney or central nervous system (CNS) effects.

Medical/First Aid

Personnel who work with HDI polyisocyanates should have a complete pre-placement medical examination and periodic (at least annual) examinations thereafter, including a pulmonary function test. It is advisable that pulmonary function testing be administered before placement in an isocyanate area to establish a baseline — then two weeks and again two months after starting work. Following that, pulmonary function testing should be repeated routinely at six months or yearly intervals. Special, non-routine testing after a major exposure or accident is also advisable. Anyone with a medical history of chronic respiratory disease, asthma or bronchial attacks, or indications of allergic responses or recurrent eczema or sensitization conditions of the skin should not handle or work with HDI polyisocyanates.

If a worker develops respiratory distress when working with these products, he/she should be removed from exposure and be examined by a physician. If hypersensitivity to HDI polyisocyanates has developed, the worker must be removed from any further exposure to any isocyanate. At present there is no conclusive screening test suitable for detecting persons most likely to become sensitized to HDI monomer or HDI polyisocyanates. Therefore, it is essential to examine all cases of absence due to illness, especially if related to the respiratory tract, to determine an individual's ability to continue work with HDI polyisocyanate containing products. Should an individual be suspected of being sensitized, Covestro's Medical Department is available to consult with your company physician: phone 412-413-2000.

First Aid Procedures for Overexposure to HDI Polyisocyanates

- **Eyes:** Flush with clean, lukewarm water (low pressure) for at least 15 minutes, while lifting eyelids. Refer individual to physician or ophthalmologist for immediate follow-up.
- **Skin:** Remove contaminated clothing immediately. Wash affected areas thoroughly with soap and water. Wash contaminated clothing thoroughly before re-use. For severe exposures, get under safety shower after removing clothing, then get medical attention. For lesser exposures, seek medical attention if irritation develops or persists.
- **Inhalation:** Move to an area free from risk of further exposure. Administer oxygen or artificial respiration as needed. Obtain medical attention. Asthmatic-type symptoms may develop and may be immediate or delayed up to several hours. Treatment is essentially symptomatic. Consult a physician.
- **Ingestion:** Do Not Induce Vomiting. Give 1 to 2 cups of milk or water to drink. Do Not Give Anything By Mouth To An Unconscious Or Convulsing Person. Consult a physician.

Note to physician: In the event that material has gotten into the eyes, stain for evidence of corneal injury. If cornea is burned, instill antibiotic/steroid preparation frequently. Workplace vapors could produce reversible corneal epithelial edema impairing vision. This product may be a skin sensitizer. Therefore, if it has touched the skin, treat symptomatically as for contact dermatitis or thermal burn. In the case of ingestion, treat symptomatically. There is no specific antidote; inducing vomiting is contraindicated because of the irritating nature of the product. In the event of inhalation, this product may be a pulmonary sensitizer. Treatment is essentially symptomatic. An individual having a dermal or pulmonary sensitization reaction to this material must be removed from any further exposure to any isocyanate.

Toxicological Testing Data

Acute Testing — Diisocyanates/Polyisocyanates

In acute animal toxicity tests, polyisocyanates based on HDI, which contain less than 0.7% monomer, are low in oral and dermal toxicity. These products produce slight to moderate irritation to the skin and moderate eye irritation in rabbits. Acute inhalation studies, in which rats have been exposed to aerosols (spray mist) of several polyisocyanates containing HDI, resulted in 4-hour LC_{50} (concentration which resulted in death of 50% of the exposed animals) values of 137-1150 mg/m^3, placing this material in the highly toxic by inhalation range. In addition, lung irritation and edema were observed during gross pathology. Rats exposed to HDI monomer aerosols (spray mist) have shown irritation to the respiratory tract and have shown a 4 hour LC_{50} of 310-350 mg/m^3. Mice were exposed to an aerosol (spray mist) of an isocyanurate type HDI polyisocyanate (Desmodur N 3300A) mixed with acetone for three hours. The irritation potential expressed as the RD_{50} (the concentration which is predicted to reduce the respiratory rate by 50%) was 20.8 mg/m^3. Pulmonary (lung) irritation was observed first, followed by sensory (eye, nose, and throat) irritation.

Longer Term Testing — Diisocyanates/Polyisocyanates

Rats exposed to a biuret type HDI polyisocyanate (Desmodur N 3200A) at 3.7, 17.5 and 76.6 mg/m^3 for three weeks (6 hrs/day, 5 days/wk) exhibited respiratory distress and many inflamed areas of tissue in the lungs and upper respiratory tract when exposed to 17.5 mg/m^3 and above. The No Observable Effect Level (NOEL) was 3.7 mg/m^3.

Furthermore, rats were similarly exposed to an isocyanurate type HDI polyisocyanate (Desmodur N 3300A) at 4.3, 14.7 and 89.8 mg/m^3 for three weeks (6 hrs/day, 5 days/wk). Respiratory distress and inflammation of the nasal passages were observed at 14.7 mg/m^3 and above. At the 89.8 mg/m^3 level many inflamed areas of tissue in the lung were observed. The NOEL in this study was 4.3 mg/m^3.

In a subchronic animal toxicity test, rats exposed for 13 weeks (6 hrs/day, 5 days/wk) to a biuret type HDI polyisocyanate (Desmodur N 3200A) at aerosol concentrations of 0.4, 3.4 and 21 mg/m^3 exhibited lung weight increases at the highest dose. Histopathology (microscopic tissue study) revealed swelling and thickening in the lower respiratory tract as well as thickening of the broncho-alveolar areas of the lung and thickening of the septum at 21 mg/m^3. There were no effects noted in the upper and central respiratory tract. The NOEL in this study is considered to be 3.4 mg/m^3.

In another subchronic animal toxicity test, rats were exposed to an isocyanurate type HDI polyisocyanate (Desmodur N 3300A) for 13 weeks (6 hrs/day, 5 days/wk) at aerosol concentrations of 0.5, 3.3 and 26.4 mg/m^3. Body weight gain of male rats of the 26.4 mg/m^3 group was slightly reduced toward the end of the study. The lung weight to body weight ratio was significantly increased in the male and female rats of the 26.4 mg/m^3 group. Histopathologic diagnosis of these animals revealed inflammatory changes and formation of fibrous tissue at the point of injury in the respiratory tract. In addition, the lung function tests at the end of the study provided evidence of a chronic obstructive lung disorder in rats of the 26.4 mg/m^3 group. The NOEL in this study is considered to be 3.3 mg/m^3.

In a chronic, lifetime (two year) study rats were exposed by inhalation to hexamethylene diisocyanate (HDI) monomer at concentrations of 0.005, 0.025 and 0.175 ppm (TLV, 5 times the TLV and 35 times the TLV for HDI). No exposure-related increase in tumors was observed; in other words, the HDI exposure did not cause cancer in this test.

Sensitization Testing — Diisocyanates/Polyisocyanates

Animal toxicity testing has indicated that some HDI polyisocyanates may cause pulmonary (respiratory) and dermal (skin) sensitization. Evidence exists that cross-sensitization between HDI and other isocyanates, particularly TDI and hydrogenated MDI, can occur.

Mutagenicity

The Ames test involving the biuret type HDI polyisocyanate (Desmodur N 100A) was negative.

Comparison of Monomer and Polyisocyanate

For a comparison of the toxicity of the HDI monomer and HDI polyisocyanates, please see below. This comparison shows that at very high spray mist concentrations (well above the airborne concentrations typically found in the workplace), HDI polyisocyanate causes as much lung irritation in laboratory animals as does HDI monomer. However, at lower concentrations more typically found in the workplace, HDI polyisocyanate is considerably less toxic than HDI monomer.

Comparison of HDI Monomer and HDI Polyisocyanate Inhalation Toxicity

Test	HDI	HDI Polyisocyanate	Comparison
Four Hour Inhalation (LC_{50} Rat)	310-350 mg/m³	137-1150 mg/m³	Similar
Sensory Irritation (RD_{50} — Mouse)	1.3 mg/m³	21-92 mg/m³	Polyisocyanate is 16 to 71 times less irritating to upper respiratory tract
Three or Four Week Inhalation (NOEL — Rat)	0.034 mg/m³	3.7 - 4.3 mg/m³	Polyisocyanate is about 120 times less toxic
Three Month Inhalation (NOEL — Rat)	0.069 mg/m³	3.3 - 3.4 mg/m³	Polyisocyanate is about 50 times less toxic

Toxicity Testing — Solvents

Several products in this group are offered dissolved in solvents. Acute animal data are available on these solvents. Refer to the Safety Data Sheet or contact Covestro for specific information on the solvent(s) in the product(s) of interest. Covestro's Product Safety and Regulatory Affairs Department can be contacted directly by telephone at (412) 413-2835 or consult our Product Safety First website at http://www.productsafetyfirst.covestro.com/.

Handling Procedures

Since HDI polyisocyanates have the potential to irritate and sensitize, it is imperative that proper steps be taken to prevent overexposure to isocyanate-containing vapors, mists or over-spray. This includes individuals actually handling the isocyanate as well as those in the immediate vicinity.

If an individual is sensitized to isocyanates, that individual must no longer work in areas where there is potential for exposure to isocyanate vapor or mist. This is equally true of exposures to isocyanates other than the one suspected of causing the sensitization.

A distinction must be made between spray or heated applications and non-spray, non-heated procedures such as filling from one container to another or mixing the components by stirring. As indicated earlier, HDI polyisocyanates are high in acute inhalation toxicity and, as described in the **Health Effects** section on pages 2-4, they can cause respiratory irritation and possibly respiratory sensitization. However, the likelihood of overexposure in non-spray, non-heated applications is reduced due to the low volatility of HDI polyisocyanates.

To illustrate the great differences in speed of evaporation, one can compare the room temperature vapor pressures. On a relative scale, if the vapor pressure of HDI biuret polyisocyanate is assigned a value of 1, the ease of evaporation (vapor pressure) numbers would be as follows:

Chemical	Vapor Pressure in mm Hg	Relative Vapor Pressure
Desmodur N Polyisocyanate		
– Isocyanurate Trimer	5.2×10^{-9}	0.00056
– Biuret	9.3×10^{-6}	1
HDI Monomer	0.011	1200
TDI Monomer	0.025	2700
Water	18.0	1,900,000
MEK (methyl ethyl ketone solvent)	91.0	9,800,000

For non-spray, non-heated applications, the inhalation risk to non-sensitized or non-hypersensitive individuals is reduced. The likelihood of exceeding the exposure limits for HDI and the HDI polyisocyanate is low as long as the regular exchange of air is carried out as specified for handling solvents. It is advisable to provide exhaust air ventilation when opening drums in which the saturation vapor concentration could have built up over a prolonged period.

For spraying, regardless of the consideration given to monomer content, precautions must be taken to ensure that the applicator does not inhale spray mist. This applies not only to HDI polyisocyanate containing coatings, but in principle to any paint system.

Engineering Controls

Ideally, hazard control of vapor or spray mist is performed through engineering controls. Effective engineering controls should be used whenever possible to reduce and/or eliminate worker exposure to all respiratory hazards.

There are several engineering controls available to reduce exposure to vapors and mists generated by the use of these products. The most common is a properly designed and ventilated enclosure. General dilution ventilation, local exhaust ventilation, or isolation may prove adequate under certain conditions. By adequate we mean ventilation sufficient to keep airborne concentrations of contaminants below their respective TLV's, PELs and MGLs. Whenever possible, local exhaust ventilation should be provided in accordance with the guidelines in Industrial Ventilation, A Manual of Recommended Practice for Design, 29th Edition, published by the American Conference of Governmental Industrial Hygienists (ACGIH). In addition, allspray finishing operations must comply with OSHA regulations 29 CFR 1910.94(c) and 1910.107.

To reduce environmental contamination, exhausted air may need to be cleaned by means of filters or scrubbers.

Use of alternative application equipment (e.g., airless or electrostatic spray equipment) may help reduce spray mist generation during spray painting. In addition, the use of spray gun extenders may help reduce the amount of spray mist in the breathing zone of the painter.

As discussed in the **Health Effects** case on pages 2-4, and earlier in this section, the likelihood of overexposure in non-spray, non-heated applications of coatings containing HDI polyisocyanates is reduced due to the low volatility of these materials. Hence, the use of brush, roller, squeegee, curtain or roll coating application reduces the likelihood of inhalation overexposure.

Periodic monitoring of the workplace should be conducted to ensure that airborne concentrations of contaminants are being controlled below their respective exposure limits (see **Monitoring** on page 13).

In addition, periodic airflow measurements for the spray booths and other local exhaust ventilation should be obtained in order to verify effectiveness. A means of continually or periodically checking the airflow of the spray booths should be investigated; suggestions include: mounting a velometer to the booth, or mounting a manometer or static pressure gauge to measure the pressure drop across the filters. As dry filters get dirty, the pressure drop increases and the air flow rate is reduced. Determination of the most suitable control measure is dependent upon the specific application.

Personal Protection — Inhalation

It is recognized that exhaust ventilation or other engineering or administrative controls must first be determined and implemented whenever feasible to control airborne concentrations of solvents, HDI polyisocyanates and other components of the coating. Personal protective equipment also must be considered. Use of personal protective equipment, especially respirators, can be very effective in minimizing potential health hazards encountered during the application of paints.

Since high solvent vapor concentrations may present both health and fire/explosion hazards, proper ventilation and respiratory protection may be necessary even if airborne isocyanate concentrations are below the appropriate TLV, PEL, and MGL (refer to the Safety Data Sheet for the specific product). Measurement of airborne contaminants should be performed at the start up of the operations and periodically thereafter to assure continued effective control of potential inhalation hazards. Refer to *Patty's Industrial Hygiene and Toxicology* — Volume I (3rd edition), Chapter 17; and Volume III (1st edition), Chapter 3 for guidance concerning appropriate air sampling strategy to determine airborne contaminant concentrations (see **Monitoring** on page 13).

In the event that airborne contaminants are not being controlled below the appropriate TLV, PEL and MGL, respiratory protection is mandatory. The basic purpose of any respirator is to protect the respiratory system (nose, throat, mouth, lungs) from harmful airborne physical or chemical agents. Many of today's coatings contain substances which, if inhaled even in minut quantities, may cause acute or chronic effects to the respiratory tract or other parts of the body. Respirators can provide protection from these hazards in either of two ways: by supplying an independent source of breathable air (fresh air-supplied respirator) or by removing the contaminant from the air before it is inhaled (air-purifying respirator).

Regarding odor warning properties it is important to note that pure HDI polyisocyanates and HDI monomer have odor thresholds that are higher than the TLV, PEL or MGL. Thus, if a vapor/particulate air-purifying respirator has exceeded its service life, breakthrough of the filter can result in exposure over the allowable limit without the wearer being able to smell the isocyanate.

The appropriate selection and use of a respirator is an important part of protection from work-related chemical hazards. When applying or handling HDI polyisocyanates, a respirator that is recommended or approved for use in isocyanate containing environments (air-purifying or fresh air-supplied) may be necessary; consider the type of application and environmental concentrations. However, the job of respiratory protection is not completed with the purchase of the respirator. Whenever respirators of any type are used, there must be a respirator program which complies with the Occupational Safety and Health Administration minimum requirements (29 CFR 1910.134). The following are some of the factors that must be taken into consideration:

- Users must be medically approved to wear respirators.
- Users of respirators must be properly trained in their selection, use, and maintenance.
- Users must always be sure the respirator is in good working order.
- Users must know the respirator's limitations. With respect to air-purifying respirators, change prefilter and carbon element (cartridge) as needed; if it is a disposable unit, know when to dispose of it.
- Users must be sure the respirator fits properly.
- Multiple use respirators must be cleaned after each use.
- The air source for a supplied air respirator must be protected from contamination. If compressor air is used, filters and monitors are needed to maintain breathable air standards. If a free standing air pump is used, the intake must be placed where it will pick up clean air.

Respirator manufacturers may be helpful in developing a good respirator program.

Whenever a coating system is spray-applied, it is essential that the applicator be protected from inhalation of both vapors and spray mists (aerosols) by use of the appropriate respirator. Aerosolized droplets from coatings contain all coating ingredients which may include: pigments, solvents, resins, additives and polymeric material. In addition, two-component reactive polyurethane coatings based on products discussed in this booklet contain unreacted HDI monomer and HDI polyisocyanate. Each of these components will have its own physiological effect on the individual.

A respirator that is recommended or approved for use in isocyanate-containing environments (air-purifying or fresh air-supplied) may be necessary for spray applications or other situations such as high temperature use which may produce inhalation exposures. A supplied air respirator (either positive pressure or continuous flow type) is recommended. Before an air-purifying respirator can be used, air monitoring must be performed to measure airborne concentrations of HDI monomer and HDI polyisocyanates. Specific conditions under which air-purifying respirators can be used are outlined in the following sections.

Respirator Guidelines for Spray Application

Good industrial hygiene practice dictates that when isocyanate based coatings are spray applied, some form of respiratory protection should be worn. During the spray application of coatings containing this product, the use of a supplied-air (either positive pressure or continuous flow type) respirator is mandatory when one or more of the following conditions exists:

- The airborne isocyanate concentrations are not known; or
- The airborne isocyanate monomer concentrations exceed 0.05 ppm averaged over eight (8) hours (10 times the 8 hour TWA exposure limit); or
- The airborne polyisocyanate (polymeric, oligomeric) concentrations exceed 5 mg/m^3 averaged over 8 hours or 10 mg/m^3 averaged over 15 minutes (10 times the 8 hour TWA or the 15 minute STEL exposure limits); or
- Operations are performed in a confined space (see OSHA Confined Space Standard, 29 CFR 1910.146).

A properly fitted air-purifying (combination organic vapor and particulate) respirator, proven by test to be effective in isocyanate-containing spray paint environments, and used in accordance with all recommendations made by the manufacturer, can be used when all of the following conditions are met:

- The airborne isocyanate monomer concentrations are known to be below 0.05 ppm averaged over eight (8) hours (10 times the 8 hour TWA exposure limit); and
- The airborne polyisocyanate (polymeric, oligomeric) concentrations are known to be below 5 mg/m^3 averaged over 8 hours or 10 mg/m^3 averaged over 15 minutes (10 times the 8 hour TWA or the 15 minute STEL exposure limits); and
- A NIOSH-certified End of Service Life Indicator or a change schedule based upon objective information or data is used to ensure that cartridges are replaced before the end of their service life. In addition, prefilters should be changed whenever breathing resistance increases due to particulate buildup.

Respirator Guidelines for Non-Spray Operations

During non-spray operations such as mixing, batch making, brush or roller application, etc., at elevated temperatures (for example, heating of material or application to a hot substrate), it is possible to be exposed to airborne isocyanate vapors. Therefore, when the coatings system will be applied in a non-spray manner, a supplied-air (either positive pressure or continuous flow-type) respirator is mandatory when one or more of the following conditions exists:

- The airborne isocyanate concentrations are not known; or
- The airborne isocyanate monomer concentrations exceed 0.05 ppm averaged over eight (8) hours (10 times the 8 hour TWA exposure limit); or
- The airborne polyisocyanate (polymeric, oligomeric) concentrations exceed 5 mg/m^3 averaged over 8 hours or 10 mg/m^3 averaged over 15 minutes (10 times the 8 hour TWA or the 15 minutes STEL exposure limits); or
- Operations are performed in a confined space (see OSHA Confined Space Standard, 29 CFR 1910.146).

A properly fitted air-purifying (combination organic vapor and particulate) respirator, proven by test to be effective in isocyanate-containing spray paint environments, and used in accordance with all recommendations made by the manufacturer, can be used when ALL of the following conditions are met:

- The airborne concentrations of the isocyanate monomer are below 0.05 ppm averaged over eight (8) hours (10 times the 8 hour TWA exposure limit); and
- The airborne polyisocyanate (polymeric, oligomeric) concentrations are known to be below 5 mg/m^3 averaged over 8 hours or 10 mg/m^3 averaged over 15 minutes (10 times the 8 hour TWA or the 15 minute STEL exposure limits); and
- A NIOSH-certified End of Service Life Indicator or a change schedule based upon objective information or data is used to ensure that cartridges are replaced before the end of their service life. In addition, prefilters should be changed whenever breathing resistance increases due to particulate buildup.

Personal Protection — Eyes

In addition to respirators, it is suggested that, for purposes of eye protection, safety glasses, chemical goggles or a full face shield be worn when working with a coating.

Personal Protection — Skin

Exposed skin areas should be covered with clothing (including permeation resistant gloves, preferably constructed of butyl rubber, nitrile rubber, or neoprene) or barrier skin creams, since a cured coating cannot be easily removed from unprotected skin. By applying a protective skin cream before beginning work with polyurethane paints, adhering splashes of paint can be more easily removed with soap and water. Skin areas covered only by protective creams should be kept to an absolute minimum. Organic solvents should not be used for skin-cleaning since they wash oils out of the skin and can cause secondary reactions. If paint is accidentally splashed onto the skin, the worker should stop work immediately and scrub it off with soap and water. If some paint does cure onto the skin, it is better to let it wear off than to try to remove it by drastic means such as harsh solvents.

Guidance Concerning Protective Coveralls:

Coverall Suggestions for Painters

Conditions	Types of Coveralls
– Intermittent Spraying – Good Ventilation – Small Amount of Overspray – No Splash Potential	Tyvek®, Kimberly Clark KleenGuard® GP, Kappler Pro/Shield 1 or equivalent
– Continuous Spray – Moderate Amount of Overspray – Moderate Splash Potential – Potential to Rub Against Freshly Painted Surfaces	Tyvek® QC, Kimberly Clark KleenGuard® FP, Kappler Pro/Shield 2 or equivalent
– Heavy and Continuous Overspray – Heavy Splash Potential – Coverall surface becomes thoroughly wetted with paint	Saranex 23P-Coated Tyvek® or Kappler Pro/Shield 3 or equivalent

In any case, a method to check whether one has the proper level of protection is to periodically examine the inside of the suit looking for any color or stickiness indicating paint penetration or permeation (note: to prevent dermal contact with HDI or its prepolymers, use a gloved hand for this examination.) An alternative is to use an analytical method such as Swype test patches to test for isocyanate contamination on the inside of the coverall. If there is evidence of breakthrough, use of the next more protective level of coverall is indicated. Swypes can be purchased from Colorimetric Laboratories, Inc., Des Plaines, IL. Phone: 847-803-3737

Monitoring

As discussed earlier, the monitoring of the workplace air to determine concentrations of contaminants including isocyanates and solvents is a key step in determining the effectiveness of engineering controls as well as in determining the type of respiratory protection required.

In order to determine the airborne levels of isocyanates, monitoring of the environment is required. Specific sampling and analytical techniques have been developed to determine these levels.

At present, the Covestro preferred method for sampling and analysis of HDI polyisocyanates in spray applications is Covestro Method 1.4.4. Samples are collected using impingers containing 2 x 10^{-4} M N-(4-nitrobenzyl)-propylamine (nitroreagent) in toluene. Analysis is by high performance liquid chromatography (HPLC) and ultraviolet detection at 254 nanometers.

For situations in which only HDI monomer vapors would be present, such as in non-spray handling and use, the 1-(2-pyridyl)piperazine impregnated glass fiber filter with analysis by HPLC, Covestro Method 1.7.6, is recommended. Based on our experience, high temperatures appear to cause the 1-(2-pyridyl)piperazine to be driven off the filter possibly resulting in an under reporting of airborne HDI. Hence, sampling times should be kept as short as possible. Sampling for 60 minutes at 81°F and 50% relative humidity resulted in loss of one half of the reagent.

Continuous or direct reading monitors for HDI monomer vapors have been developed. It must be pointed out, however, that these units may not be suitable for monitoring in spray application environments. These instruments may provide information as to airborne HDI monomer vapor concentrations during non-spray applications such as: mixing, repackaging, batchmaking, coil coating, and brush/roller/squeegee application. Covestro is not aware of a direct reading instrument which can be used to accurately determine airborne concentrations of HDI polyisocyanates.

Information concerning direct reading HDI vapor monitors can be obtained from: Honeywell Analytics, 405 Barclay Blvd., Lincolnhshire, IL 60069, 1 (888) 955-3973, detectgas@Honeywell.com, or Bacharach Inc., 621 Hunt Valley Circle, New Kensington, PA 15068, (724) 334-5000, Help@MyBacharach.com.

Reactivity and Decomposition Hazards

HDI polyisocyanates are reactive with compounds which contain active hydrogen, (e.g., water, ammonia, amines and alcohols). Strong bases, such as tertiary amines, caustic soda and potash can catalyze the reaction with these compounds, as well as other reactions, and the result can be uncontrolled polymerization. The heat and products generated from this reaction can result in a pressure build-up in closed containers which may be sufficient to rupture the vessel. HDI polyisocyanates react slowly with water to liberate carbon dioxide gas (CO_2); under confined conditions in closed containers, explosive rupture of the vessel has occurred. If water contamination is suspected, do not reseal the container or vessel. Containers

used to package HDI polyisocyanate products must be dry, clean and airtight. If you notice a buldging drum, call Chemtrec at 1 (800) 424-9300 for assistance.

Burning of any material can produce irritating and/or toxic fumes. The multitude of materials present in a product or present in the immediate area, and their synergistic or additive effects can complicate the determination of smoke toxicity.

In a fire situation, whenever HDI polyisocyanate, or a polyurethane derived from it, is burned, HDI monomer vapors and other toxic, potentially lethal fumes and gases (e.g., carbon monoxide, carbon dioxide, oxides of nitrogen and hydrogen cyanide) can be generated. Fire fighters must wear self-contained breathing apparatus, in addition to protective clothing, including rubber coats, boots, gloves, and helmet. Large fires involving these materials can be extinguished with water spray. However, water should be used in very great quantities and with proper care since the reaction between water and hot isocyanate may be vigorous. High expansion (proteinic) chemical extinguishers (e.g., monoammonium phosphate, potassium sulfate, potassium chloride) can be used for smaller fires.

When welding or cutting steel, coated with a polyurethane system, the worker is exposed to decomposition products (metal fumes, gases or vapors, particulate) which vary depending on type of process being used to weld or cut, nature of the base metal, and type of coating system. One or more of the following control procedures should be used for welding or cutting steel coated or in contact with a polyurethane system:

- Use a power brush or grinding wheel to strip coating from steel in the vicinity where cut or weld is to be made. A well-fitted dust respirator with N95 or better filters and eye protection should be used while stripping the paint.
- Use a local exhaust hood to remove fumes during the welding or cutting operation.
- Use a fresh air-supplied respirator during welding or cutting.

Spill Clean-Up Procedures

In preparation for accidental spills, it is advisable to have a written procedure for dealing with such an emergency. A designated emergency team, perhaps part of the fire team, may be appropriate.

A number of factors will affect the extent of the hazard associated with a spill: the amount spilled, volatility and flammability of the material, the temperature of the material and the location of the spill.

Spill Control Procedure

Overriding Principle: 1) Protect people first, 2) Prevent or minimize any environmental releases, 3) Finally, protect property and product.

1. Identify Material(s)
2. Evacuate area, and remove ignition sources
   - Size of evacuation area depends on type of material, temperature and size of spill.
3. Notify supervision and others as necessary.
4. Put on Personal Protective Equipment (PPE)
   - Respirator (Consult SDS)
   - Face and eye protection
   - Permeation resistant gloves
   - Permeation resistant suit.

5. Shut off source (where applicable).
6. Dike the spill (where applicable)

   Note: Steps 7-12 are for small spills (10 gallons or less). For larger spills, call Chemtrec 1 (800) 424-9300

7. Absorb and decontaminate
   - Oil-dry or similar absorbent
   - Decontaminating solution:
   - 20% Union Carbide Tergitol TMN-10 or other nonionic surfactant which is liquid and mixes well with water.
   - 80% water.
8. Remove, treat, and discard absorbent/decontaminant mixture.
   - After 15 minutes, shovel absorbent into steel drum and place outside, covered loosely, for 72 hours. This material may be a hazardous waste. For example, it may have a flash point less than 140°F if it contains an organic solvent. The HDI polyisocyanate reacts with water to produce a low toxicity polyurea (see **Waste Disposal Section** on page 16).
9. Decontaminate surface
   - Scrub with more decontaminant solution.
10. Decontaminate and remove protective equipment.
11. Return to normal operation.
12. Do accident investigation.

During routine transfer of HDI polyisocyanate in which minute amounts of material may drip from a valve, a pan containing the above described premixed solution of absorbent and decontaminant should be placed under the valve.

Leaking Containers

When possible, leaking containers should be turned so that the damaged area of the drum is facing up, and should be covered to protect against rain, dirt or other contamination. Further, leaking containers should be clearly marked or segregated as such. Any spillage should be dealt with as described above (see **Spill Control Procedure** on page 14). If the contents are still usable, transfer them to a clean, dry undamaged container. If the contents are not usable, the leaking container and contents should be placed in an overpack container.

Empty Containers

“Empty” non-returnable containers will contain residual material. All labeled precautions for the material itself must be observed when handling these containers.

Used containers should not be distributed to anyone but a professional reconditioner or disposer who is aware of relevant health and environmental precautions and chemical nature of the isocyanate component. A Safety Data Sheet should be sent along with the containers so the reconditioner or disposer will have information on the container’s contents. The use of drum dealers, scrap dealers, and open dumps is strongly discouraged. Reconditioned drums are to be used for industrial purposes only. No such container should be used for personal purposes (e.g., trash burning, grill pits, water collection and/or

storage, etc.). Do not apply heat, sparks, or open flame (electric or gas torch) to the empty container. Irritating and highly toxic decomposition products can be formed (see **Reactivity and Decomposition Hazards** on page 13).

In normal unloading operations, isocyanate containing materials drained from tank cars and tank wagons are replaced by dry air or nitrogen. Empty tankers padded with dry air or nitrogen should be sealed with all gaskets in place and all valves tightly closed and returned to the supplier. Under no circumstances should personnel enter any "empty" tank car, tank wagon, holding tank, or storage vessel until all safe tank entry procedures have been completed.

Waste Disposal

The Resource Conservation and Recovery Act of 1976 (RCRA) requires safe management of hazardous wastes, which are defined to include solid, liquid, semi-solid, and gaseous materials. The applicable regulations are contained in 40 CFR parts 260-272. These regulations include EPA's identification and listing of Hazardous Wastes (40 CFR Part 261).

Presently, HDI polyisocyanates are not specifically listed as hazardous wastes. However, wastes may also be defined as hazardous waste due to certain physical or chemical characteristics defined in Section 261.20-24. Several HDI based polyisocyanate products contain solvents which reduce the flash point of the product below 140°F. These products, if discarded, are defined as ignitable hazardous waste.

Other HDI based polyisocyanate products (e.g., Desmodur N 75A BA/X) contain solvents, such as xylene, which may contain trace amounts of benzene. Liquid products which contain benzene at levels greater than 0.5 mg/liter, if discarded, are defined as hazardous waste under the Toxicity Characteristic Leaching Procedure (TCLP). For example, Desmodur N 75A BA/X, which contains 12.5 weight percent xylene, may contain up to 0.55 mg/liter benzene. This calculation is based on our xylene supplier's determination of the amount of benzene in his product. Of course, an HDI polyisocyanate product which contains more than 12.5 weight percent xylene would contain proportionately more benzene. None of the HDI polyisocyanates meet either of the remaining characteristics — corrosivity or reactivity. These characteristics may be defined differently in individual state regulations. Any processing of these products may, however, result in reclassification of any resultant waste material.

Incineration of organic materials in appropriately designed and licensed incinerators is the preferred method of waste management. However, regardless of the disposal method, it is recommended that the operation be inspected by responsible personnel to determine whether the disposer can properly and safely handle the container and dispose of any waste.

Regulations may differ from state to state. Your regional EPA office or your state environmental agency can be helpful in interpreting the law and identifying approved disposers and reconditioners. Covestro does not have analytical facilities to evaluate waste, nor can Covestro accept waste for treatment, storage, and/or disposal. However, if information is required, your Covestro account manager can put you in touch with the appropriate Covestro technical group for assistance in identifying:

- Commercial hazardous waste management firms
- Commercial drum reconditioners
- State environmental regulatory agencies

Summary

Other sources of information pertaining to HDI polyisocyanates include the product specific Safety Data Sheets, product data sheets and labels.

Covestro also offers a wide range of brochures, booklets and videos that are available in the Information Resources page on Covestro's Product Safety First website (http://www.productsafetyfirst.covestro.com). For further assistance on accessing documents to fit your specific needs, please contact your Covestro Representative.

When working with HDI polyisocyanates, you should:

- Become informed and aware of the hazards and appropriate control procedures. Read the product literature, the Safety Data Sheet, and the label. If you are a manufacturer of resins or coatings, talk with your raw materials supplier; if you are a paint applicator, talk with the company supplying the paint.
- Provide a medical program and monitor the workplace environment.
- Follow recommendations prescribed for use during handling and during application. This includes use of adequate ventilation, protective clothing, eye protection, and respirators.
- Observe proper storage conditions and disposal procedures.
- For assistance in using HDI polyisocyanates, contact Covestro's Product Safety and Regulatory Affairs Department at (412) 413-2835.

References

Industrial Ventilation: A Manual of Recommended Practice; American Conference of Governmental Industrial Hygienists.

29 CFR 1910.94 OSHA General Industry Standard on Ventilation.

29 CFR 1910.107 OSHA General Industry Standard on Spray Finishing Using Flammable and Combustible Materials.

29 CFR 1910.134 OSHA General Industry Standard on Respiratory Protection.

40 CFR, Part 261, Identification and Listing of Hazardous Waste.

CHEMTREC Emergency Telephone Numbers:

- USA (800) 424-9300
- International (703) 527-3887

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1 Covestro Circle
Pittsburgh, PA 15205 USA
412-413-3983

www.productsafetyfirst.covestro.com
CAS_NA@covestro.com

The manner in which you use, and the purpose to which you put and utilize our products, technical assistance and information (whether verbal, written or by way of product evaluations), including any suggested formulations and recommendations, are beyond our control. Therefore, it is imperative that you test our products, technical assistance and information to determine, to your own satisfaction and requirements, whether our products, technical assistance and information are suitable for your intended uses and applications. This application-specific analysis must at least include testing to determine suitability from a technical as well as health, safety, and environmental standpoints. Such testing has not necessarily been done by Covestro.

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